

Quantum Zeno-based control mechanism for molecular fragmentation

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A quantum control mechanism is proposed for molecular fragmentation processes within a scenario grounded on the quantum Zeno effect. In particular, we focus on the van der Waals Ne-Br₂ complex, which displays two competing dissociation channels via vibrational and electronic predissociation. Accordingly, realistic three dimensional wave packet simulations are carried out by using *ab initio* interaction potentials recently obtained to reproduce available experimental data. Two numerical models to simulate the repeated measurements are reported and analyzed. It is found that the otherwise fast vibrational predissociation is slowed down in favor of the slow electronic (double fragmentation) predissociation, which is enhanced by several orders of magnitude. Based on these theoretical predictions, some hints to experimentalists to confirm their validity are also proposed.

The quantum Zeno effect (QZE) was theoretically predicted in 1977 by Misra and Sudarshan¹ and experimentally observed by Itano *et al.*² almost 15 years later. The opposite phenomenon, the so-called anti-Zeno effect (AZE), was later on predicted^{3,4} and observed immediately afterwards.⁵ These are well-known phenomena in the literature of quantum theory of measurement and open quantum systems, mainly in connection with decoherence processes.⁶ If a series of successive observations or measurements are carried out on an unstable system at very short time intervals τ , its decay can be either inhibited (QZE) or accelerated (AZE). These two remarkable behaviors with time become apparent when looking at the *survival probability* $P(t)$, namely the probability to find the system in the same initial state, $|\psi(0)\rangle$, at a certain subsequent time t ,

$$P(t) = |\langle\psi(0)|\psi(t)\rangle|^2 = |\langle\psi(0)|e^{-i\hat{H}t/\hbar}|\psi(0)\rangle|^2. \quad (1)$$

Here, $\hat{H} = \hat{H}_0 + \hat{V}$ encompasses the system free-evolution Hamiltonian, \hat{H}_0 , and the system interaction, \hat{V} . Because of the continuous measurement (or projection) process, the system decay can be described, in general, as³

$$P(t) \sim e^{-\gamma(\tau)t}, \quad (2)$$

where $\gamma(\tau)$ is the measured-modified decay rate, which depends on τ . This rate is different from the free-measurement system decay rate, γ_0 . The decay rate $\gamma(\tau)$ can be expressed³ in terms of the spectral density of final states, $G(\omega)$, and the measured-induced initial state level width, $F(\omega; \tau)$, as

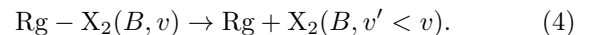
$$\gamma(\tau) = 2\pi \int_0^\infty G(\omega)F(\omega; \tau)d\omega. \quad (3)$$

The measurement frequency $\nu = 1/\tau$ is related to the initial state energy uncertainty, ΔE , as $\Delta E/\nu \sim \hbar$. Hence, the decay rate is essentially determined by the spectral density profile within a bandwidth ν around its energy level. According to Kofman and Kurizki,³ Eq. (3) constitutes a universal result: frequent measurements on a given initial state generally lead to its dephasing through randomization of the corresponding phase. Depending on whether ν is much larger or much shorter than the

spectral density width with respect to the center of gravity of $G(\omega)$, either QZE or AZE is expected, respectively. In this regard, 1D systems have been largely considered theoretically,^{8,9} while multidimensional realistic systems are almost unexplored. Furthermore, Kofman and Kurizki¹⁰ have already discussed the idea of using QZE to control the decay rate of quantum systems coupled to a continuum reservoir by means of weak perturbations. The experiment carried out by Fischer *et al.*,⁵ with cold atoms initially trapped in an optical lattice, precisely shows the appearance of QZE and AZE by repeatedly on/off switching of the coupling between an almost bound state and a continuum. On the other hand, it has also been shown¹¹ that periodic coherent pulses acting between the decaying level and an auxiliary one, can either inhibit or accelerate the decay into a reservoir. In chemical reactivity, evidences of AZE have been shown by Prezhdho,¹² who also considered this mechanism as a novel route to quantum controlling in chemistry. This is a step towards the control of decoherence and entanglement in molecular systems which can handle large amounts of quantum information.^{13–15}

In this work, on the contrary, a mechanism is proposed to quantum controlling the time-evolution of several competing fragmentation processes of an isolated molecule in gas phase, based on the QZE. Thus, by doing repeated measurements on one of the dissociation channels the outcome of an unimolecular fragmentation can be controlled. Isolated molecular systems allow to interpret experimental results based on realistic multidimensional models, allowing accurate quantum dynamical studies.

To this end, rare gas-halogen diatom van der Waals complexes (Rg-X₂) are ideal systems displaying a natural separation between the fast intramolecular X₂ vibration and the slow intramolecular Rg-X₂ motions.⁷ The van der Waals (vdW) complex is prepared in the *B* excited electronic and vibrational *v* state, Rg-X₂(*B*, *v*), by the optical *B* ← *X* electronic transition. The vibrational energy, initially deposited in the X₂ subunit, flows towards the weak Rg-X₂ mode producing the fragmentation through vibrational predissociation (VP),



The dissociation process is monitored by detecting the

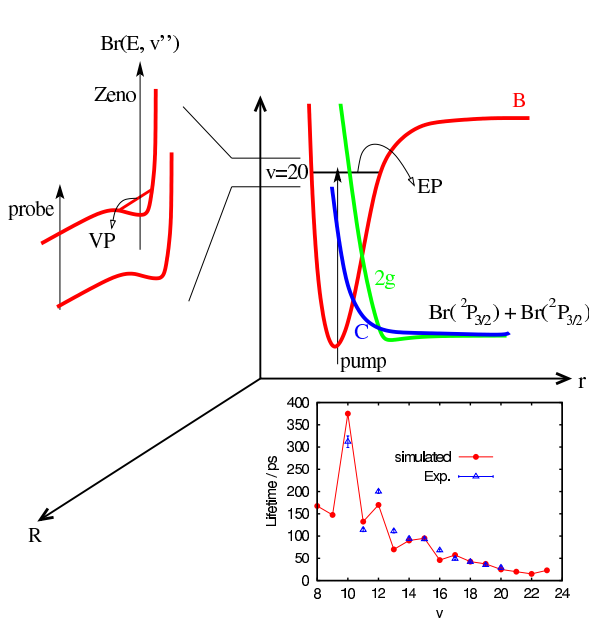
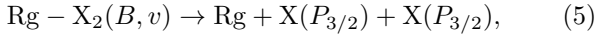


FIG. 1: Schematics of the VP/EP fragmentation process considered here, including the pump/probe and Zeno-type pulses (see text for details). In the inset, measured¹⁷ and simulated¹⁶ total lifetimes.

$X_2(B, v')$ fragments by a second probe laser. The presence of the Rg atom induces electronic couplings in the X_2 subunit. This may eventually produce electronic pre-dissociation (EP) via double fragmentation,



indicated schematically in Fig. 1. This process was first detected for Ar-I₂ complex.^{19–22} The Ne-Br₂ system constitutes a benchmark since the existing VP/EP competition has been extensively studied. Numerical results obtained using 3D potential energy surfaces issued from *ab initio* calculations¹⁶ have been found to be in excellent agreement with experimental complex lifetimes,¹⁷ as seen in the inset of Fig. 1. In this figure, oscillations are attributed to the EP process due to the Frank-Condon factors between the electronic B state and the dissociative 2_g and C states of Br₂. As expected from the energy gap law,¹⁸ the VP rate increases monotonically with v ; for $v > 15$, it becomes more efficient and dominates. Based on the excellent realistic model describing the experimental results, here we study the NeBr₂($B, v=20$) decay using 3D wave packet (WP) simulations under frequent measurements. As is shown below, this allows us to slow down the otherwise dominant VP for $v=20$ in favor of the slower EP, which involves two different dissociative electronic states, the 2_g and C states of Br₂.

Let us first only consider the VP process for Ne-Br₂($B, v=20$) in order to illustrate the QZE and AZE. This is carried out by expanding the WP as²³

$$|\Psi(t)\rangle = \sum_{v'} \Phi_{v'}(R, \theta, t) \varphi_{v'}(r). \quad (6)$$

Here, $\varphi_{v'}(r)$ denote the vibrational eigenfunctions of the Br₂(B) subunit; $\Phi_{v'}(R, \theta, t)$ depends on the distance R between Ne and the Br₂ center-of-mass and the angle θ between the two Jacobi vectors, \mathbf{r} and \mathbf{R} . The pre-dissociation lifetimes are of the order of 10-100 picoseconds, while the quadratic behavior of the decay occurs at a much shorter time scale (of the order of femtoseconds or shorter). The inclusion of a new pulse (Zeno pulse in Fig. 1) in the propagation is computationally very demanding, and a first order perturbation approach is adopted for simplicity to deal with the corresponding absorption. Within this approximation, the effect of the Zeno pulse can be described by two limiting cases. First, the population depletion method, where the pulse fully promotes the dissociative $\Phi_{v-1}(R, \theta, t)$ component of the WP to a higher electronic state by optical pumping. This is simulated by projecting the WP on the different vibrational states and then removing the $v-1$ component at each measure time $n\tau$. Second, the dephasing or randomization method where the measurement introduces a random phase in the $\Phi_{v-1}(R, \theta, t)$ component as a perturbation, simulated by multiplying $\Phi_{v-1}(R, \theta, t)$ by a random phase depending on the coordinates R and θ .

The effect of these two measurement schemes on $P(t)$ can be explained by formally expanding the WP as

$$|\Psi(t)\rangle = a_b(t)e^{-iE_b t/\hbar}|b\rangle + \sum_f a_f(t)e^{-iE_f t/\hbar}|f\rangle, \quad (7)$$

where $|b\rangle$ and $|f\rangle$ denote the initial bound state and final dissociative states of \hat{H}_0 , respectively. At very short times, the decay of $|b\rangle$ into some final $|f\rangle$ is described by first-order perturbation theory as²⁴

$$\frac{da_b}{dt} = -\frac{i}{\hbar} \sum_f V_{bf} a_f e^{-i(E_b - E_f)t/\hbar}. \quad (8)$$

By means of a series of repeated measurements at time intervals $\tau \rightarrow 0$, it is possible to freeze the evolution of the initial state, slowing down the transition by destroying the coherence on the right-hand side of Eq. (8) (Ref. 25) (for each (R, θ) pair, there is a given positive/negative sign for the probability amplitude and the integrated amplitude vanishes). As seen in Fig. 2, the typical QZE and AZE behavior is numerically reproduced for Ne-Br₂($B, v=20$) using the randomization model with different values for τ . With the depopulation method nearly indistinguishable results are also obtained, demonstrating the robustness of the approximations made. When considering repeated measurements with short τ , the lifetime increases by an order of magnitude, from 27 ps in the free (unperturbed) case to about 320 ps in the case of $\tau=5$ fs. A similar deceleration is also found for $\tau < 50$ fs. This is a clear manifestation of the QZE. For $\tau = 100$ fs, the lifetime is 20 ps, approximately the same as in the free case, while for $\tau > 100$ fs, VP is enhanced, yielding a lifetime of 13 fs, according to the AZE. The exponential decays for different values of τ fulfill the predicted behavior given by Eq. (2). In Fig. 2 the fittings to that

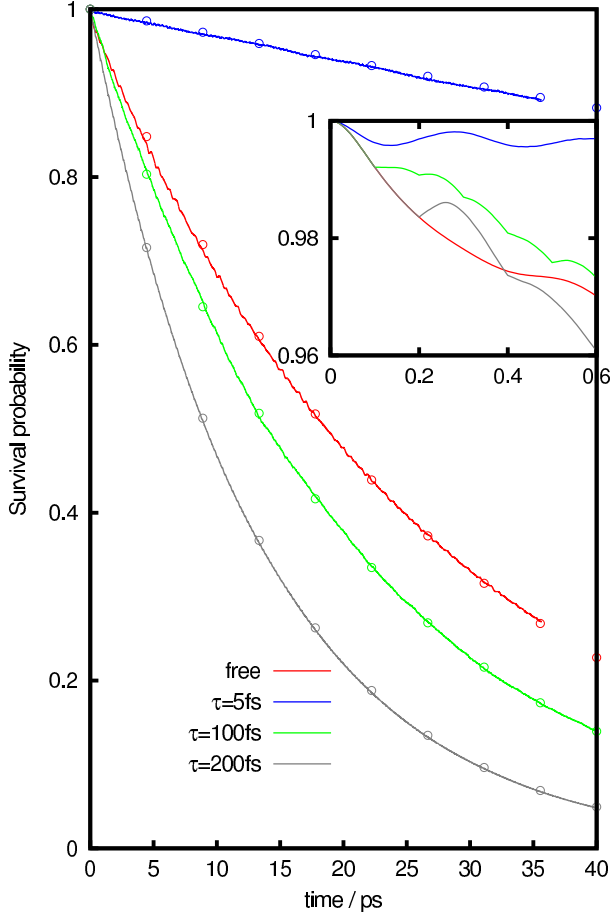


FIG. 2: Survival probability as a function of time for the free (unperturbed) evolution (red) and using different time intervals τ for the randomization procedure. In the inset, enlargement on the short-time dynamical regime. Open circles are fits to the exponential decay of Eq. 2, with $\gamma_0 = 0.098$ (free) and $\gamma(\tau) = 0.008$ ($\tau=5$ fs), 0.13 ($\tau=100$ fs) and 0.199 ($\tau=200$ fs), all given in cm^{-1} .

expression are shown with open circles. The QZE is only found for short values of τ , where the decay is quadratic. The Zeno behavior is lost after 0.1-0.2 ps, just when the curvature of the free population changes. It should be noticed that the $v-1$ dissociative component of the WP is measured instead of the initial v component. However, the usual QZE and AZE behaviors are found. This is easily understood within the randomization measurement model. The dissociation in this case is slowed down by introducing a random phase difference between the bound and dissociative components of the WP. Such a difference can be applied either to the initial, v , or dissociative, $v-1$, component, leading to the same results, when only one fragmentation channel is considered.

In the case of several fragmentation channels, measuring the initial state would slow down the total decay towards all the dissociation channels. On the contrary, measuring one of the dissociative states, would slow down selectively a given dissociation channel leaving nearly un-

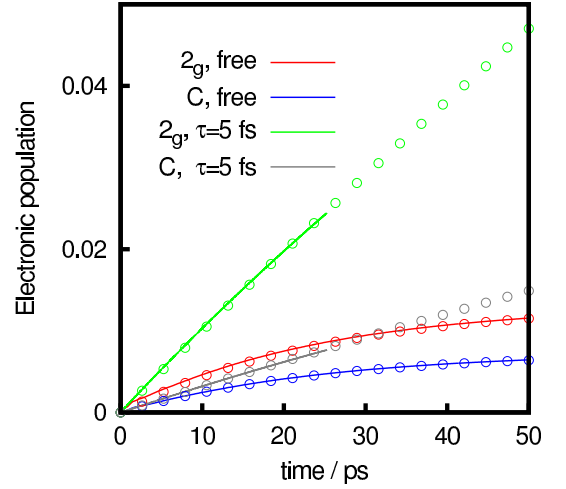


FIG. 3: Electronic populations of the 2_g and C dissociative states of the Br_2 as a function of time, due to EP for the free dynamics and under repeated measurements with $\tau=5$ fs. Solid lines correspond to numerical calculations. Open circles correspond to fittings of the form $Q_\alpha^\tau(1-e^{-\gamma(\tau)t})$, with $\gamma_0=0.106 \text{ cm}^{-1}$, $\gamma(\tau=5 \text{ fs})=0.0083 \text{ cm}^{-1}$. The branching ratios are $Q_{2g}^0=0.0133$, $Q_C^0=0.0074$, $Q_{2g}^5=0.325$ and $Q_C^5=0.103$.

changed the other ones. This scenario is precisely the one used here when considering the competition of the VP channel described above together with the EP channel towards the 2_g and C dissociative states of Br_2 . It is therefore expected that the slow electronic fragmentation described by Eq. (5) can be enhanced by slowing down the dominant VP channel. To deal with the two dissociation mechanisms, the total WP is written as²⁶

$$|\Psi(t)\rangle = \sum_{\alpha} \Phi_{\alpha}(r, R, \theta, t) \chi_{\alpha}, \quad (9)$$

where χ_{α} ($\alpha = B, 2_g$ and C) is the electronic wave function and $\Phi_{\alpha}(r, R, \theta)$ is expanded on a grid of $256 \times 160 \times 40$ points for the three Jacobi coordinates.¹⁶ Due to the large grid involved, the calculations have been parallelized in the angle θ .²⁶ The randomization model employed above becomes unstable numerically for long times. For this reason, the measurements are simulated by the depopulation method, by projecting the $\Phi_{\alpha=B}(r, R, \theta)$ component onto the initial state, removing all other possible contributions describing the VP dynamics at each τ . The typical QZE oscillations are again observed as in the previous case. The slowing down effect introduced by the repeated measurements is again remarkably reproduced and rather important. Since the VP process is slowed down, the whole lifetime increases.

Under such conditions, EP rates become larger or of the same order than VP ones. Thus, the electronic population for the two dissociative electronic channels increases. In Fig. 3 the electronic population of the Br_2 2_g and C dissociative states, is displayed as a function of time. An analytical fitting to the exponential law is also

shown; the electronic branching ratios are obtained from this fitting. The branching ratio of the 2_g state changes from 1.3% in the free case to 32.5% with repeated measurements every $\tau=5$ fs; for the C state, this ratio changes from 0.74% to 10.3%. This implies the branching ratios of these two states increase by factors 25 and 14, respectively. This is a clear evidence of how the Zeno pulse can slow down the otherwise dominant VP, producing an important enhancement of EP, which leads to a total $\text{Br}+\text{Br}+\text{Ne}$ fragmentation.

For the particular case studied here, experiments could be performed by simply adding a third pulse, the Zeno-pulse, to the usual pump-probe experiment.¹⁷ The frequency of this Zeno-pulse should be tuned into the $B \rightarrow E$ transition maximizing the absorption intensity. It is expected that the intensity should be high to promote the population of the $(B, v-1)$ channel as much as possible. The Zeno-pulses should be short, of the order of 1 fs in order to allow a measurement frequency ν of the order of 0.2 fs^{-1} . The relative phase of the pulses are not expected to play a major role since the (coherent or incoherent) dynamics on the upper E state is not of interest here. These effects should hold for $\tau \rightarrow 0$, and it can be envisaged to use a continuous laser to generate the Zeno pulse, as recently proposed by Kurizky and co-workers²⁷ in a different context. In this way, the direct detection of EP products, namely the atomic $\text{Br}(^2P_{3/2})$ fragments would allow to measure EP rates directly in absence or by diminishing VP. Thus, the oscillations of EP rates as a function of v associated with the electronic

$B/2g$ or B/C Frank-Condon factors could then be better interpreted. This could help to unravel the complex dynamics in other similar systems, such as the prototypical Ar-I_2 .²⁸ This working scheme will also allow the other way around, that is, to enhance VP in cases where EP is dominant, such as for $v=11$ in NeBr_2 .

In summary, the QZE-based control mechanism is of rather general applicability, and only requires two competing decay channels. By acting on one of them, by slowing down or accelerating it using the QZE or AZE, respectively, one can obtain a change of the branching ratios of one or two orders of magnitude. This quantum control method is specially well adapted for slow decay dynamics, where other control methods requiring coherence fails, such as the coherence control method. When including the Zeno-pulse in the simulations, there may be an attenuation of the processes described, but the results obtained are expected to be rather robust and will not change the major physics here proposed.

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